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Journal of Polymer Science, Part B

Polymer Letters

Editorial Board: R. M. Fuoss • J. J. Hermans • H. Mark • H. W. Melville • C. G. Overberger • G. Smets

Contents

WALDEMAR SILBERSZYC: Unperturbed Dimensions of Polyoxymethylene 577

H. L. FRISCH: Factorization of the Activation Energies of Permeation and Diffusion of Gases in Polymers 581

C. GEACINTOV, R. S. SCHOTLAND, and R. B. MILES: Phase Transition of Crystalline Polybutene-1 in Form III 587

HARVEY ALTER: Polymer Microscopy and Morphology by an Improved Technique 593

KENNETH F. O'DRISCOLL and PAUL J. WHITE: Kinetics of Polymerization of Styrene Initiated by Substituted Benzoyl Peroxides. I. Effect of Thermal Initiation 597

A. TURNER and F. E. BAILEY, JR.: An Apparent Anomaly in the Glass Transition of Polyisobutylene 601

LUIS G. ROLDAN and HERMAN S. KAUFMAN: Crystallization of Nylon 6 603

C. H. BAMFORD and A. D. JENKINS: Zero Points in Schemes of Radical Reactivity .. 609

DONALD R. SCHULTZ: Anaerobic Polymerization of Vinyl Monomer–Trialkylborane Mixtures 613

G. S. PARK: Gamma Irradiated Crosslinked Cellulose 617

ARTHUR E. WOODWARD: Comparison of Solubility Data for Irradiated Polypropylene 621

continued inside

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Journal of Polymer Science **Part B: Polymer Letters**

Editorial Board:
R. M. Fuoss • J. J. Hermans • H. Mark • H. W. Melville • C. G. Overberger • G. Smets

Contents (continued), Volume 1, No. 11

R. J. Alexander and J. R. Doyle: Polysulfones of Norbornadiene 625

Matahumi Ishibashi: Polymorphism in Poly-*p*-Ethylene Oxybenzoate 629

Yutaka Sakurada, Masakazu Matsumoto, Kiyokazu Imai, Atsuo Nishioka, and Yoshinori Kato: Proton Magnetic Resonance Spectra of Poly-α-Methylstyrene 633

Hans Coll and F. H. Stross: Transient Osmotic Effects 641

John N. Lomonte: The Infrared Spectrum of Ethylene-Propylene Copolymers and the Determination of Propylene Content 645

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UNPERTURBED DIMENSIONS OF POLYOXYMETHYLENE

In their recent review of intrinsic viscosities and unperturbed dimensions of chain molecules, Kurata and Stockmayer (1) called attention to an apparently unique situation in the case of polyoxymethylene. Finding no suitable viscosity data for this polymer, they referred to the measurements by Uchida, Kurita, and Kubo (2) of the dipole moments of the ethers $CH_3OCH_2OCH_3$ and $CH_3(OCH_2)_2OCH_3$. The latter authors concluded that the gauche (skew) conformation of each internal rotational angle was more stable than the trans conformation by about 1.74 kcal./mole. Kurata and Stockmayer converted this number into a value of 0.61 for the dimensionless ratio

$$\sigma = [\langle L^2 \rangle_o / \langle L^2 \rangle_{of}]^{1/2} \qquad (1)$$

where $\langle L^2 \rangle_o$ is the unperturbed mean square end-to-end distance of the chain and $\langle L^2 \rangle_{of}$ is the value which the mean square length would have if all internal rotations were completely unhindered. Since all other polymers thus far studied have σ-values greater than unity, this low figure for polyoxymethylene would have great interest if it were real. The purpose of this letter is to show that the correct value is surely much larger and quite similar to that for most polymers.

It is easy to verify that the Kurata-Stockmayer figure is obtained only when all the internal rotations are assumed completely independent of each other. As is well known, this model permits the occurrence of "pentane interferences" which should be excluded as sterically very unfavorable, and which correspond to the conformational sequences GG′ and G′G. For chains in which the trans conformation is energetically favored, the error made by assuming independent rotations may remain modest, but if the gauche conformation becomes more stable this is a very serious flaw. Indeed, as Uchida, Kurita, and Kubo clearly point out, the pentane interferences then cause the chain to take on helical sequences which may be quite long with an energy difference of the magnitude given by them for polyoxymethylene. The probability of continuing a gauche sequence is

$$p = 1/[1 + \exp(-\Delta E/RT)] \qquad (2)$$

and with ΔE = 1.74 kcal./mole we get p equal to 0.950 at 25°C. and 0.890 at 145°C. The corresponding weight-average lengths of helical sequences at these two temperatures are 39 and 17 bonds, respectively.

We may now apply another relation given by Kurata and Stockmayer to

obtain a more realistic estimate of σ. If the occasional trans bonds are ignored, their eq. (97) may be used in the form

$$\langle L^2 \rangle_o = nrb_o^2 \tag{3}$$

where n is the number of bonds in the chain, r is the weight average length of a helical sequence and b_o is the translation distance per bond along the helical axis. If we assume for simplicity, as did Uchida et al., that there are exactly four bonds per turn of the helix and that the valence angles are exactly tetrahedral, we have $b_o^2 = l^2/3$, where l is the bond length. Since also $\langle L^2 \rangle_{of} = 2nl^2$, this gives

$$\sigma^2 = r/6 \tag{4}$$

and with the sequence lengths given earlier we get $\sigma = 2.5$ at room temperature and about 1.7 at 145°C.

A crude but satisfying confirmation of a rather normal value of σ for polyoxymethylene can be based on some old viscosity data given by Staudinger and co-workers (3). For example, a polyoxymethylene dimethyl ether with a number-average molecular weight of 3000 by end-group analysis gave a specific viscosity of 0.23 in 3% solution in formamide at 145°C. The corresponding intrinsic viscosity is about 0.075 dl./g. If we assume $a_\eta \leq 1.1$ and $\bar{M}_v \leq 2\bar{M}_n$, which are certainly reasonable upper limits for this sample, we obtain

$$K = [\eta]/\bar{M}_v^{1/2} a_\eta^3 \geq 8 \times 10^{-4} \tag{5}$$

in the customary units. With $\Phi = 2.8 \times 10^{21}$, this leads to

$$\sigma = (K/\Phi)^{1/3} M^{1/2} \langle L^2 \rangle_{of}^{-1/2} \geq 1.3 \tag{6}$$

and the true number might well be higher because of some draining effect on the viscosity for this relatively short chain.

In conclusion, it is seen that the electrostatically favored gauche conformations need not give rise to abnormally small chain dimensions if the important steric effects are taken into account. It is therefore possible that helical sequences may occur in the case of other dissolved polymers. Birstein and Ptitsyn (4), for example, have suggested that dissolved atactic polystyrene contains such structures.

The writer thanks W. H. Stockmayer for a useful soliloquy.

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FACTORIZATION OF THE ACTIVATION ENERGIES OF PERMEATION AND DIFFUSION OF GASES IN POLYMERS

While reviewing, in a different context, fairly extensive tables of activation energies for permeation and diffusion of so-called "permanent" gases in a variety of polymers, compiled by Rogers (1) and Barrer (2) respectively, we noted an empirical, numerical coincidence: Let E(i,P) be the activation energy for permeation or diffusion of gas i in polymer P, then the ratio

$$r_i = E(i,P)/E(N_2,P) = r_i(N_2,P) \qquad (1)$$

is roughly constant, independently of the polymer P employed, for each gas i and the ratio

$$R_P = E(i,P)/E(i,P_0) = R_P(i,P_0) \qquad (2)$$

is also roughly constant, independently of the gas i employed, for each polymer P with P_0 butyl rubber (BuR) in the case of permeation and German Perbunan (G.P.) in the case of diffusion. The choice of the ubiquitously studied N_2 as the reference gas was made to make the tables of r_i as extensive as possible. The reference polymers were chosen again to allow as extensive a comparison as possible and possessed r_i values (based on N_2) which were apparently in best agreement with the average value over all polymers studied, $\langle r_i \rangle_P$. While the compilation of activation energies for diffusion, made by Barrer (2), consists essentially of elastomers above their glass temperature (T_g), the compilation of activation energies of permeation (around 25°C.), given by Rogers (1), contains a number of crystalline and glassy polymers. Tables I and II exhibit the ratio $r_i(N_2,P)$ and $R_P(i,BuR)$, respectively, for permeation, while Tables III and IV exhibit the ratios $r_i(N_2,P)$ and $R_P(i,G.P.)$, respectively, for diffusion.

In view of the experimental errors in absolute (rather than relative) measurements of activation energies on different membranes we feel that the data presented in Tables I–IV support our empirical observation; with possibly somewhat better statistical likelihood in the case of diffusion in elastomers than permeation in a greater variety of polymers. It should be noted that in the case of certain cellulosic membranes where anomalies are expected (3,4) and bakelite (1) the r_i values are anomalous, e.g., r_{H_2} (N_2, Bakelite) = 0.485, r_{CO_2} (N_2, Ethocell 610) = 0.34. This suggests that the constancy of r_i (and R_P) is a consequence of the usual penetrant-polymer diffusion mechanism as described by Barrer (2).

TABLE I

r_i (N_2,P) Values for Permeation of Gases in Polymers
(Data from Reference (1))

P	i				
	H_2	H_e	N_2	O_2	CO_2
Polybutadiene	0.804	–	1.00	0.865	0.634
Perbunan 18	0.728	0.687	1.00	0.869	0.707
German Perbunan	0.694	0.614	1.00	0.851	0.710
Hycar OR 25	0.666	0.602	1.00	0.853	0.731
Hycar OR 15	0.637	0.558	1.00	0.869	0.762
Buna – S	0.781	0.758	1.00	0.838	0.655
Natural rubber	0.766	0.700	1.00	0.796	0.678
Polyisoprene 74% Acrylonitrile 26%	0.607	0.506	1.00	0.846	0.833
Polyisoprene 74% Methacrylonitrile 26%	0.632	–	1.00	0.859	0.789
Pliofilm – FM	0.560	–	1.00	0.840	0.860
Methyl rubber	0.601	0.495	1.00	0.849	0.842
Neoprene	0.763	–	1.00	0.934	0.801
Polyisobutylene 98% Isoprene 2%	0.740	0.617	1.00	0.836	0.789
Butyl rubber	0.697	0.607	1.00	0.856	0.792
Polyethylene (0.922 g./ml.)	0.699	0.709	1.00	0.880	0.701
Teflon FEP	0.864	0.673	1.00	0.794	–
Vulcaprene	0.738	–	1.00	0.887	0.770
Nylon	0.722	–	1.00	0.928	0.866
Mylar	0.732	0.613	1.00	0.853	0.826
$\langle r_i \rangle_P$	0.695	0.623	1.00	0.856	0.753
Standard Deviation (S.D.)	0.08	0.07	0.0	0.04	0.08

The simplest interpretation of the constancy of the ratios given by eqs. (1) and (2) is the hypothesis that the activation energies for diffusion or permeation factor into a product of two functions, the first function $g^{(\alpha)}(i)$ characterizing solely the gas i, the second function $h^{(\alpha)}(P)$ characterizing solely the polymer P, with the superscript (α) standing for diffusion or permeation. Thus

$$E^{(\alpha)}(i,P) = g^{(\alpha)}(i)h^{(\alpha)}(P) \qquad (3)$$

TABLE II

R_P (i,BuR) Values for Permeation of Gases in Polymers
(Data From Reference (1))

P	i						
	H_2	He	N_2	O_2	CO_2	$<R_P>_i$	S.D.
Polybutadiene	0.759	–	0.656	0.664	0.525	0.651	0.095
Perbunan 18	0.827	0.895	0.792	0.804	0.707	0.805	0.09
German Perbunan	0.910	0.921	0.912	0.906	0.818	0.893	0.04
Hycar OR 25	0.942	0.974	0.984	0.981	0.909	0.958	0.03
Hycar OR 15	1.011	1.013	1.104	1.121	1.060	1.062	0.05
Buna – S	0.782	0.868	0.696	0.682	0.576	0.721	0.10
Natural rubber	0.793	0.829	0.720	0.664	0.616	0.724	0.09
Polyisoprene 74% Acrylonitrile 26%	1.046	1.000	1.200	1.187	1.267	1.139	0.11
Polyisoprene 74% Methacrylonitrile 26%	0.931	–	1.020	1.028	1.020	1.000	0.045
Pliofilm – FM	0.640	–	0.800	0.785	0.869	0.774	0.09
Methyl rubber	0.919	0.868	1.064	1.056	1.131	1.008	0.11
Neoprene	0.931	–	0.848	0.925	0.859	0.891	0.04
Polyisobutylene	1.092	1.039	1.024	1.000	1.020	1.035	0.03
Butyl rubber	1.00	1.00	1.00	1.00	1.00	1.00	0.0
Polyethylene (0.922 g./ml.)	0.942	1.092	0.936	0.962	0.828	0.952	0.9
Polyvinyl chloride Polyvinyl acetate	0.850	0.947	0.984	0.906	0.828	0.903	0.65
Saran	–	–	1.344	1.486	1.242	1.352	0.125
Kel – F	0.816	–	1.000	1.019	0.747	0.896	0.13
Kel – F (30% cryst.)	–	–	1.144	1.047	1.191	1.126	0.07
Teflon – FEP	0.724	0.645	0.584	0.542	–	0.624	0.08
Vulcaprene	1.034	–	0.976	1.019	0.949	0.995	0.04
Nylon	0.931	–	0.896	0.972	0.980	0.945	0.04
Mylar	0.632	0.605	0.600	0.598	0.628	0.612	0.015

TABLE III

r_i (N_2,P) Values for Diffusion of Gases in Polymers
(Data From Reference (2))

P	i					
	He	H_2	A	O_2	N_2	CO_2
Polybutadiene	–	0.708	–	0.944	1.00	1.014
Perbunan 18	0.494	0.718	–	0.953	1.00	1.082
Natural rubber	0.494	0.690	–	0.954	1.00	1.023
Butadiene-styrene copolymer	–	–	1.011	–	1.00	–
German Perbunan	0.500	0.663	–	0.885	1.00	1.029
Polymethylpentadiene	–	–	–	0.883	1.00	–
Butadiene-methylmethacrylate copolymer	–	–	0.896	–	1.00	–
Isoprene-methacrylonitrile copolymer	–	0.595	–	0.827	1.00	1.052
Hycar OR 25	0.444	0.598	–	0.880	1.00	1.025
Vulcaprene A	–	0.650	–	0.872	1.00	1.008
Neoprene (vulcanized)	–	0.770	0.983	–	1.00	–
Butyl rubber	0.479	0.669	–	0.983	1.00	0.992
Hycar OR 15	0.433	0.598	–	0.858	1.00	1.055
Isoprene-acrylonitrile copolymer	0.338	0.510	–	0.876	1.00	0.993
Methyl rubber	–	0.605	–	0.895	1.00	1.032
$\langle r_i \rangle_P$	0.454	0.648	0.963	0.901	1.00	1.028
S.D.	0.03	0.07	0.065	0.04	0.0	0.03

TABLE IV

R_P (i,G.P.) Values for Diffusion of Gases in Polymers
(Data From Reference (2))

P	i						
	He	H_2	O_2	N_2	CO_2	$\langle R_P \rangle_i$	S.D.
Polybutadiene	–	0.739	0.739	0.692	0.682	0.713	0.03
Perbunan 18	0.807	0.898	0.880	0.817	0.860	0.852	0.04
Natural rubber	0.827	0.870	0.902	0.837	0.832	0.854	0.03
Butadiene-styrene copolymer	–	–	–	0.856	–	–	–
German Perbunan	1.00	1.00	1.00	1.00	1.00	1.00	0.0
Polymethylpentadiene	–	–	1.065	1.067	–	1.066	0.001
Butadiene-methylmethacrylate copolymer	–	–	–	1.106	–	–	–
Butadiene-acrylonitrile copolymer	–	–	–	1.106	–	–	–
Isoprene-methacrylonitrile copolymer	–	1.000	1.043	1.115	1.140	1.074	0.065
Hycar OR 25	1.000	1.014	1.120	1.125	1.121	1.076	0.06
Vulcaprene A	–	1.101	1.108	1.125	1.103	1.109	0.01
Neoprene (vulcanized)	–	1.340	–	1.144	–	1.242	0.01
Butyl rubber	1.115	1.174	1.293	1.163	1.121	1.173	0.07
Hycar OR 15	1.057	1.101	1.185	1.221	1.252	1.163	0.08
Isoprene-acrylonitrile copolymer	0.942	1.072	1.138	1.394	1.346	1.178	0.18
Methyl rubber	–	1.087	1.206	1.192	1.196	1.170	0.06

with

$$r_i^{(\alpha)}(i_0,P) = g^{(\alpha)}(i)/g^{(\alpha)}(i_0)$$

and

$$R_P^{(\alpha)}(i,P_0) = h^{(\alpha)}(P)/h^{(\alpha)}(P_0)$$

The additive relationship connecting the $E^{(\alpha)}(i,P)$ with ΔH_s, the apparent heat of solution of the gas in the polymer, together with eq. (3) would imply that ΔH_s has either one of the general forms

$$\Delta H_s(i,P) = f_1(i)\,h(P) \tag{4}$$

with $h^{(\alpha)}(P) = h(P)$ or

$$\Delta H_s(i,P) = g(i)\,f_2(P) \tag{5}$$

with $g^{(\alpha)}(i) = g(i)$, where $f_1(i)$ is a function characterizing solely the gas i and $f_2(P)$ a function characterizing solely the polymer P. The strong conditions on ΔH_s expressed by eqs. (4) or (5) immediately suggest possible restrictions on the general validity of the basic relations contained in eqs. (1)–(3). In any case, these observations may prove to have some utility in simplifying future more general corresponding state treatment of these transport processes.

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PHASE TRANSITION OF CRYSTALLINE POLYBUTENE-1 IN FORM III

Isotactic polybutene-1 was successfully synthesized by Natta and his co-workers (1) in 1954. The characteristically polymorphous behavior of polybutene-1 has evoked a great deal of interest (2), and the existence of two distinct crystalline modifications was recognized at an early date: a metastable form crystallizing from the melt (form II) and a stable form (form I) which is formed upon standing or by subjecting the polymer in the form II modification to pressure or stretching. More recently, a third crystalline modification (form III) (3,4) was obtained by precipitating polybutene-1 from solution, but very little information beyond the fact that polybutene-1 in the form III modification is stable at room temperature had been available until Danusso and Gianotti (4) re-

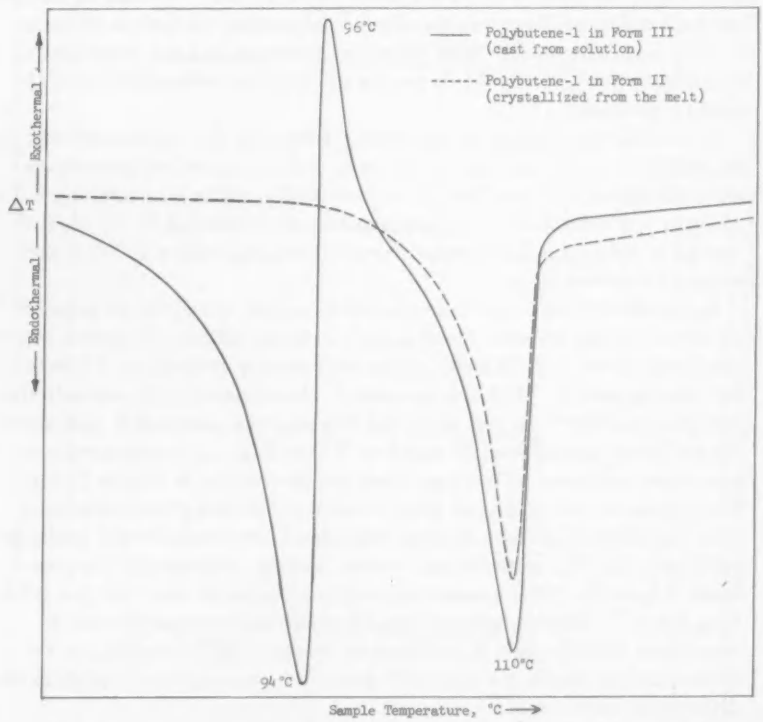

Fig. 1. DTA thermogram of polybutene-1 form III to form II phase transition. (Heating rate: 1.6°C./min.)

ported on the dilatometric and thermodynamic fusion properties of the three morphological forms of isotactic polybutene-1.

We wish to report on some novel methods of preparing polybutene-1 in the form III modification, as well as on some interesting observations we have made on the properties of this particular crystalline modification of polybutene-1. Our data were obtained using a polybutene-1 which was 96% insoluble in boiling ether and had an intrinsic viscosity $[\eta] = 1.52$ at 60°C. in n-heptane.

Polybutene-1 in the form III crystalline modification can be obtained by freeze-drying a 10-20% benzene solution of polybutene-1 on a high vacuum line. After all the solvent has been flashed off, polybutene-1 is recovered as a spongy white polymer which gives the characteristic x-ray diffraction pattern of the form III modification (3,4). Casting of polybutene-1 films from toluene or carbon tetrachloride solutions at room temperature also results in the formation of the form III modification. The preferred method is to cast the films from carbon tetrachloride solution onto glass plates using a Gardner Ultra Applicator to spread out the film. Other solvents such as p-xylene, decalin, etc., may also be used, although the crystalline modification of polybutene-1 which is ultimately obtained, is dependent upon the type of solvent and the temperature treatment which is followed during the casting and subsequent crystallization process.

An interesting property of polybutene-1 films in the crystalline form III modification is that they are not only stable at room temperature as reported earlier, but that form III is essentially stable to stretching and pressure application at room temperatures, as evidenced by the lack of change in infrared spectra and differential thermal analysis (DTA) thermograms obtained by us.

Polybutene-1 films cast from toluene or carbon tetrachloride solution as described above, were found to give an x-ray diffraction pattern characteristic of the form III modification without any indication of another form being present. DTA measurements were apparently in contradiction with this finding, however, since the thermograms presumably indicated the presence of both form III and form II (see Fig. 1) in approximately equivalent amounts. (For comparison the dotted line in Figure 2 is a thermogram of the melting of polybutene-1 in the form II modification.) It is immediately obvious that the presence of two endothermic peaks at 94°C. and 110°C., respectively, cannot both be attributed to the presence of form III. This apparent discrepancy between our x-ray and DTA data led us to assume that the form III modification of polybutene-1 transforms into the form II modification in the 94-96°C. region, as evidenced by the exothermic crystallization or "rearrangement" peak in the differential curve at 96°C. (Fig. 1).

This assumption was confirmed by heating a polybutene-1 sample in the form III modification in an x-ray diffraction unit, and observing the

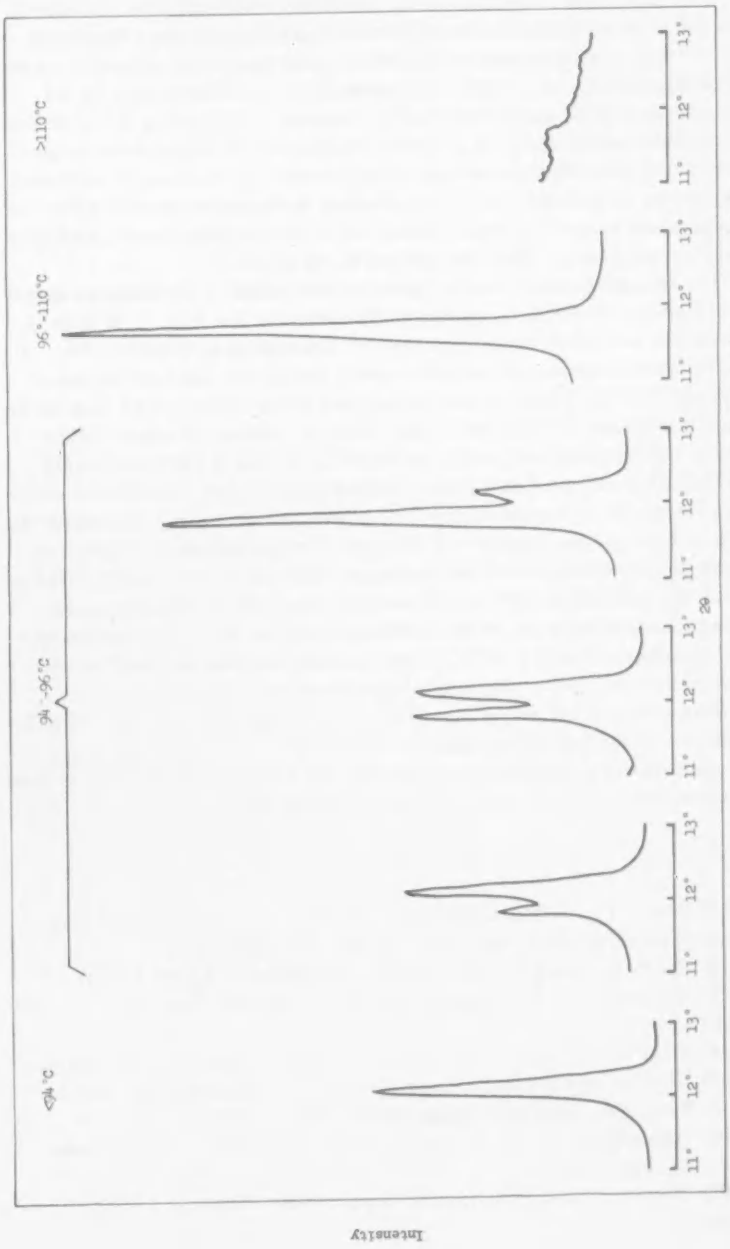

Fig. 2. X-ray diffraction pattern of polybutene-1 form III to form II phase transition.

resulting patterns at temperature intervals as shown in Figure 2. The well-defined peak characteristic of form III at angle $2\theta = 12.1°$ is observed at temperatures below 94°C. At higher temperatures the intensity of this peak was seen to diminish rapidly and simultaneously a new peak appeared at $2\theta = 11.8°$, this latter peak is characteristic of the form II crystalline modification of polybutene-1. If heating is continued, both peaks are recorded as a doublet over a narrow temperature range (94-96°C.), followed by the total disappearance of the form III peak and emergence of a single peak corresponding to form II in the 96-110°C. temperature range. At temperatures above the melting point of form II, only an amorphous diffraction pattern is recorded.

The observed transformation goes to completion in the range of only a few degrees (94-96°C.). Further confirmation of the form III to form II transition was obtained by dilatometric measurements (heating rate 0.1°C./min.) resulting in melting curves having two distinct breaks at 103 and 115°C. These breaks correspond to the transition of form III to form II and form II to the melt, respectively. The exact nature of the phase transformation occurring at 94-96°C. (DTA) is not immediately evident from the available data; presumably this transformation is either an example of neocrystallization (5) of the type occurring in gutta percha (6), or it is another instance of the type of transition occurring in 1,4-trans-polybutadiene which, according to Natta and Corradini (7), Nikitin et al. (8) and Dannis (9), is a first-order transition in the solid state. The presence, however, of an exothermic peak at 96°C. in addition to the endothermic peak at 94°C. might indicate melting followed by recrystallization, rather than one single phase transformation.

More detailed investigations of the morphology and properties of polybutene-1 in the crystalline form III modification are under way in our laboratories to establish more precisely the nature of the form III to form II transition and the results will be presented soon.

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POLYMER MICROSCOPY AND MORPHOLOGY BY AN IMPROVED TECHNIQUE

Microscopic examination of polymers, their morphology under polarized light, in particular, requires the use of thin film samples at known temperatures. An improved technique is reported whereby very thin films (much less than 1 μ) of known thickness of polymer can be examined with great acuity at readily controlled temperatures.

The polymer sample is deposited as a thin film on a highly polished metal surface and examined in a metallurgical microscope with vertical illumination. The metal surface may be ferrotype plate, front surface mirror, or any convenient metal highly polished by usual metallurgical procedures. It is usually easier to deposit a thin film on the reflective backing than it is to form a sufficiently thin self-supporting film or to prepare a thin polymer film on a microscope slide mounted under a cover slip. The polymer film is coated on the metal backing by dipping the substrate into an appropriate solution. Film thickness is controlled by the withdrawal rate from solution, concentration and temperature of the solution, and the number of dips. More than one dip is possible if the solvent is completely evaporated between dips. A shortcoming of this technique is that it is not known what effect strong adhesion to the substrate (i.e., restriction in two dimensions) will have on the polymer morphology.

The use of a metal substrate for the polymer film permits good heat transfer and temperature control during deposition, crystallization, annealing, and hot stage work. The temperature response of thin metal backings on heating and cooling is almost immediate.

Polarized light is conveniently employed with this technique, similar to metallurgical examinations. Dayton reports (1) that the use of polarized light for examination of opaque substances was as early as 1909 (2) and now polarized light is a standard accessory to the metallurgical microscope. Analysis of the optics of combining vertical illumination with polarizer and analyzer indicates this is an appropriate system for morphological examination of polymer films provided the plane of polarization is exactly parallel or perpendicular to the microscope axis and that the metal substrate is highly polished and flat to the microscope axis. Both precautions minimize the amount of elliptically polarized light reflected from the surface so that a dark field can be obtained with the analyzer (1).

The thickness of a polymer film on a reflective backing may be measured by interferometric methods (3). The film is either deposited over a mask or scratched through to the metal surface to form a step. The step

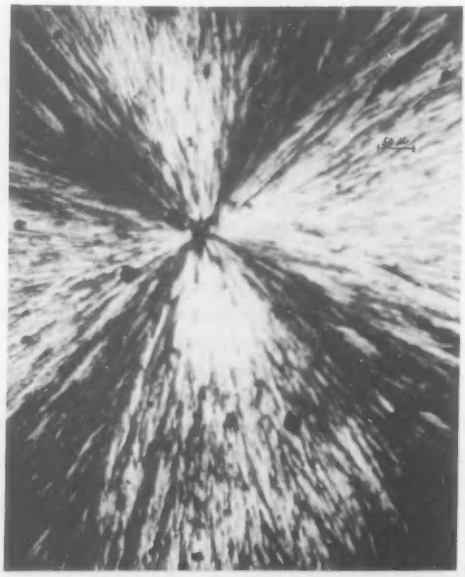

Fig. 1. Polymethylene oxide, 0.3 μ thick.

Fig. 2. Polyethylene oxide, 0.3 μ thick.

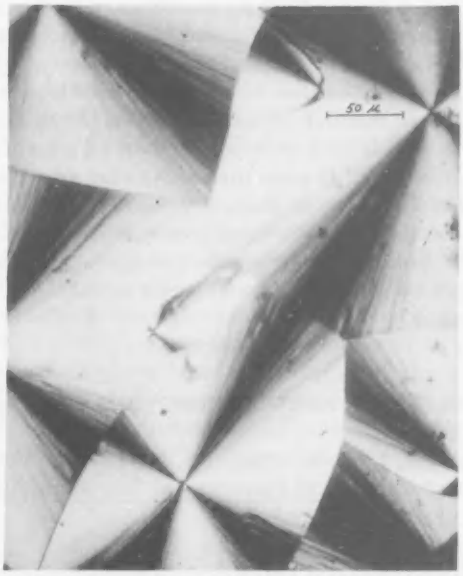

Fig. 3. Isotactic polypropylene oxide, 0.3 μ thick.

height is measured by the shift in the interference fringes observed with an interference microscope, a special interference objective (Bausch & Lomb) mounted on the metallurgical microscope, or the Nomarski polarization interferometer (Reichert) mounted between the microscope body tube and objective. The latter device is not always suitable for highly birefringent films.

Many polymers have been examined using vertical illumination of films. All of the structual features of spherulites reported in the literature have been observed, such as banded spherulites, fibrillar structures, and melting and growing patterns. The vertical illumination method was used to obtain Figures 1-3, photomicrographs of 0.3 μ thick films taken through a metallurgical microscope fitted with polarizing filter in the illuminator and polaroid analyzer between the objective and eyepiece. Figure 1 is for polymethylene oxide (Delrin 500X) deposited from dimethylformamide solution. Figure 2 is a spherulite of polyethylene oxide (Polyox WSR 35) deposited from trichloroethylene. Figure 3 shows spherulites of isotactic polypropylene oxide (experimental sample) deposited from trichloroethylene solution. After solvent evaporation the films were melted and recrystallized from the melt. The optical sign of the polyethylene oxide and polypropylene oxide spherulites was positive. The polyethylene oxide spherulites in the thin film can be easily grown large enough to be visible with the naked eye. Polymer

spherulites were not observed in very thin films, less than about 0.1 μ.

With vertical illumination of a thin film on a reflective backing, the light passes through the film twice. Doubling the optical absorbing path path permits use of thinner films than might be used in transmission. The results obtained with very thin films encouraged looking for single crystal platelets of polyethylene deposited from a crystallizing bath onto a reflective substrate. In some instances, what were thought to be single crystals were observed. However, contrast was poor and they could not be photographed. The usual observation was small particles laid down in the outline of a rectangular lozenge suggestive of granular deposit on single crystals or pieces of single crystal.

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KINETICS OF POLYMERIZATION OF STYRENE INITIATED BY SUBSTITUTED BENZOYL PEROXIDES. I. EFFECT OF THERMAL INITIATION

We have recently undertaken the use of vinyl polymerization kinetics as a tool to study in detail some of its facets such as initiation or termination. With this in mind we tried to apply the "dead-end" treatment of Tobolsky (1) to the decomposition of substituted benzoyl peroxides in styrene. Reasonable kinetic measurements require that this work be done in the region of 90°C. where thermal initiation of polymerization must be considered. We have found that, when appreciable amounts of thermal polymerization are encountered, the dead-end treatment of data cannot be used. We present below a short consideration of the reason for this, and another method for analysis of data.

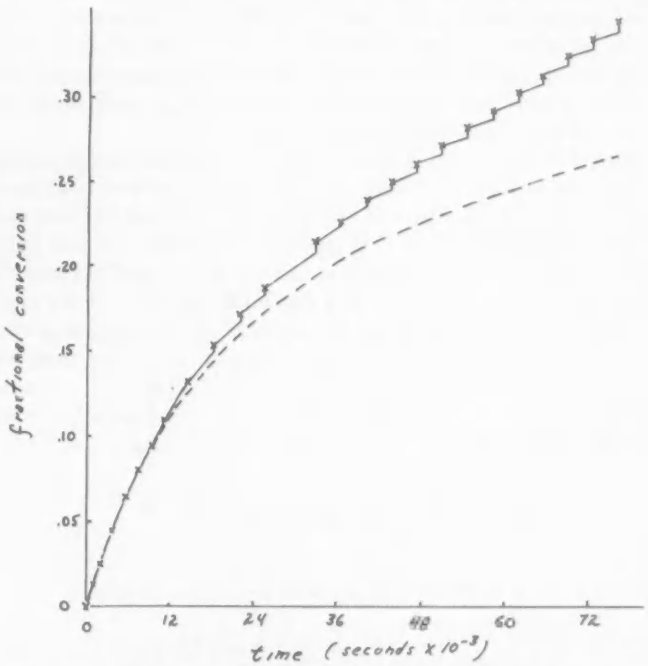

Fig. 1. Polymerization of bulk styrene at 90°C. initiated by 3.26×10^{-4} moles/liter of benzoyl peroxide. Observed conversion (×); incremental conversion due to peroxide initiation (—); cumulative conversion due to peroxide initiation (----).

Observed conversions of monomer to polymer over small time increments are best corrected for that conversion which is caused by thermal initiation. This was done by taking the square root of the difference between the squares of the observed rate of polymerization and the rate of thermal polymerization which would have occurred at the given monomer concentration in the absence of any initiator.

$$R_{p,cat} = (R^2_{p,obs} - R^2_{p,therm})^{1/2} \tag{1}$$

$R_{p,cat}$ then represents the rate of polymerization caused by "catalytic" initiation; e.g., by benzoyl peroxide. The result of this type of correction is shown graphically in Figure 1, where the ×'s represent dilatometrically observed, fractional conversions. The solid line shows the calculated change in conversion due to catalytic initiation in a time increment, while the dashed line shows the cumulative conversion due to catalytic initiation.

The dead-end treatment (1) effectively used the dashed line. This is only valid when thermal polymerization is a small fraction of the total observed polymerization. The steplike solid line, with small time increments, represents a closer approach to what is actually occurring, and must be considered, rather than the dashed line, in work such as ours, where thermal polymerization may account for as much as 20 or 30% of the observed polymerization.

In a formal mathematical sense, it must be explicitly recognized that the integration involved in the dead-end treatment assumes both monomer and catalyst concentrations to be continuous functions of time, and, therefore, of each other. The data given by the dashed line can only be an approximation which becomes more invalid as the gap between it and the solid line becomes larger. Using the solid line itself in the dead-end treatment is, of course, invalid because of its discontinuous nature.

As an alternative, when the dead-end treatment cannot be used, we have found that the following differential method (2) may be successfully applied to conversion-time data such as shown in Figure 1. Using the usual nomenclature and starting with the basic equation

$$R_{p,cat} = \frac{k_p\, k_d^{1/2}\, f^{1/2}}{k_t^{1/2}} [cat]_0^{1/2}\, [M]\, e^{-k_d t/2} \tag{2}$$

we can divide both sides by [M] and take logarithms to obtain

$$\ln\left(\frac{R_{p,cat}}{[M]}\right) = \ln\left(\frac{k_p\, k_d^{1/2}\, f^{1/2}\, [cat]_0^{1/2}}{k_t^{1/2}}\right) - \frac{1}{2} k_d t \tag{3}$$

which yields a straight line if the left-hand side is plotted versus time. From the slope and intercept the catalyst decomposition rate constant,

k_d, and efficiency, f, can be obtained if the ratio $k_p/k_t^{1/2}$ is known. This ratio is available from molecular weight studies and may be used where diffusion control of termination does not affect the ratio. Full details of this study in which the latter point is considered will be reported shortly.

Support of this work by the Petroleum Research Fund and of P. J. W. by a Special Research Assignment of the Atlantic Refining Co. is gratefully acknowledged.

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AN APPARENT ANOMALY IN THE GLASS TRANSITION OF POLYISOBUTYLENE

It has been generalized by Reding, Faucher, and Whitman (1) and by Willbourn (2) that all "vinyl" homopolymers should have main chain glass transitions at about – 25°C. due to motion of isolated $-CH_2-\underset{\displaystyle R}{\underset{|}{CH}}-CH_2-$ groups. Many vinyl polymers do not show this transition owing to steric factors or polar forces. We wish to call attention to the possibility that a similar correlation of glass transition with structure may be possible for "vinylidene" polymers but that the glass transition of polyisobutylene may be anomalous due to steric factors.

The homologous series of polyisobutylene, poly(3,3-dimethylpropane), and poly(4,4-dimethylbutane) was chosen for study. The latter two members of the series were prepared by low-temperature, alternating addition-hydride ion transfer, cationic polymerization of 3-methyl-1-butene and 4-methyl-1-pentene, respectively, according to the method of Kennedy and Thomas (3). The poly(3,3-dimethylpropane) was shown by NMR

TABLE I

Polymer	Structure	T_g (°C.)
Polyisobutylene	$-CH_2-\underset{\displaystyle CH_3}{\underset{\displaystyle \vert}{\overset{\displaystyle CH_3}{\overset{\displaystyle \vert}{C}}}}-$	–71 (Ref. 4)
Poly(3,3-dimethylpropane)	$-CH_2-CH_2-\underset{\displaystyle CH_3}{\underset{\displaystyle \vert}{\overset{\displaystyle CH_3}{\overset{\displaystyle \vert}{C}}}}-$	–10
Poly(4,4-dimethylbutane)	$-CH_2-CH_2-CH_2-\underset{\displaystyle CH_3}{\underset{\displaystyle \vert}{\overset{\displaystyle CH_3}{\overset{\displaystyle \vert}{C}}}}-$	–20

spectroscopy to be essentially pure with virtually no detectable "vinyl" polymer structure present. The poly(4,4-dimethylbutane) was found to contain over 90% of the desired structure.

The glass transition of polyisobutylene is well known (4). The transitions of the other two polymers were determined from mechanical loss measurement using a torsion pendulum, at 1 cps., similar to that described by Nielson. The values obtained are shown in Table I.

In the light of arguments advanced (1,2), the low glass transition of polyisobutylene appears out of order. An explanation for this is found in examination of the NMR spectra of the three polymers (6). In the case of polyisobutylene, the spectrum corresponding to the methyl groups is offset toward low field indicative of a high degree of hindrance. This hindrance can also be noted if molecular models of polyisobutylene are constructed. This hindrance of the methyl groups is presumably the cause of the anomalously low glass transition of polyisobutylene in this series of structures. In formulating a correlation of mechanical loss transitions with structure for "vinylidene" polymers, this apparent anomaly will have to be taken into account.

The authors are indebted to Dr. C. W. Wilson III for NMR analyses and to Dr. J. A. Faucher for mechanical loss data.

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CRYSTALLIZATION OF NYLON 6

An intensive investigation of the structure and morphology of nylon 6 (polycaprolactam) has been under way in our laboratories. X-ray diffraction, polarized optical microscopy, and density techniques have been utilized to study samples as a function of crystallinity, draw ratio, and temperature. The effects of water on the morphology are also being evaluated.

On the basis of these studies, we have established a series of structural forms which appear to be associated with nylon 6 (oriented and nonoriented). Several of these forms have previously been described by various authors; however, the determination of amorphous forms and the para-crystalline α form (in oriented samples) has, to the best of our knowledge, not been described previously. We have also developed a unified concept of the molecular order which serves to explain the interrelationships between the various phases and is consistent with our own and published data (1-5).

The forms we recognize are listed in Table I in increasing degree of structural stability. Our notations for the various forms are based on those of Bunn and co-workers (1). These are used because they follow a logical sequence as the degree of perfection of molecular order increases.

On the basis of the forms described, we suggest the following molecular picture of the nylon 6 structures.

Quenching the melt results in a loosely packed amorphous structure (amorphous 1) which on standing in the presence of moisture (which lowers the T_g) or on being warmed, stabilizes to a denser amorphous form (amorphous 2) presumably due to greater development of hydrogen bonding. When the amorphous form is heated slightly above the T_g, short range intermolecular order develops between chains, without ordering along the length of the chains. The chains may be presumed to be randomly twisted. Thus, small volume elements consisting of an assembly of cylindrically shaped molecules having a unique spacing are formed. This results in a single strong reflection characteristic of the γ pseudohexagonal form. If the chains are stretched moderately, longitudinal order of the amide groups is developed along the chain length, resulting in sharp diffraction effects in the x-ray pattern. The chain backbones, however, are not in a fixed configuration and may be partially twisted so that the amide groups make variable angles around the backbone chain. Evidence for this is noted in the x-ray diagram of the β form where disorder appears in the seventh layer corresponding to the c-c-c zig-zag distance. (2.5 A.). When viewed end-on, this produces a cylindrical

TABLE I

Structural form	Description	Characteristic spacing, A.	Density
Melt	Disordered molecular arrangement characteristic of a liquid.	4.66 (halo)	
Amorphous 1	Freshly quenched state, super-cooled liquid. Loose molecular packing.	4.3 (halo)	
Amorphous 2	Stabilized quenched state, closer molecular packaging – no order.	4.16 (halo)	1.084
γ (Pseudohexagonal), (1,5)	Nematic structure. Lateral order between chains results in a characteristic interchain spacing. No intermolecular order along chains. Twist in chains results in statistical cylindrical symmetry along the chains. Structure exhibits birefringent pattern different from that of normal spherulites.	4.13 (sharp)	1.155
β (Hexagonal), (2)	True crystalline phase only observed in oriented samples. The structure is defined by the three-dimensional ordering of the polar (amide) groups along and among chains. This requires twist in each chain which results in shortening of the identity period along the chains and a	4.10 (sharp) Unit cell a = 4.75 c = 16.75	1.150

	statistical hexagonal distribution of angles of the amide groups around the chain. Hydrogen bonding for any chain is with each of its six near neighbors which results in a three-dimensional network.		
α (px) para-Crystalline, (monoclinic)	para-Crystalline phase observed in oriented fiber samples. Unit cell dimensions are a function of sample history. The structure is defined by the position of the fully extended carbon-carbon planar zig-zag of the main chain. Chains are in planar configuration parallel to orientation direction (b axis). Planes can be in variable equilibrium positions between a and c axis which results in variable parameters of the monoclinic unit cell. Hydrogen bonding is restricted to sheet type formation. Relative position of polar groups between chains is not highly ordered. Heating this phase results in a pseudohexagonal form (due to thermal motion) which reforms to monoclinic on being cooled.	$d_{(202 + 002)} = 4.30\text{-}4.50$ $d_{(200)} = 3.70\text{-}3.86$ $\beta = 62\text{-}67^\circ$	1.136 – 1.174

(continued)

TABLE I (continued)

Structural form	Description	Characteristic spacing, A.	Density
α Bunn (monoclinic) (3),	This highly ordered crystalline phase is defined by a three-dimensional ordering of the polar groups and the fully extended carbon-carbon planar zig-zag of the main chains. This configuration requires antiparallel placement of neighboring chains and forms the closest packed structure of Nylon 6. Hydrogen bonding is in sheet form. The plane of the chain is parallel to the b axis and tends to be close to the a axis. This structure is always associated with a spherulitic morphology which may be presumed to have chain folded crystallization. Chain folding by its nature results in antiparallel chain arrangement. Heating the structure maintains monoclinic form until the melting point.	$d_{(202 + 002)} = 4.40$ $d_{(200)} = 3.70$ Unit cell a = 9.56 b = 17.2 c = 8.01 $\beta = 67.5$	1.225

projection and, consequently, a hexagonal symmetry. The chains in this form may be parallel or antiparallel since their directionality is lost due to the twist. The hydrogen bonding in the structure is multidirectional between neighboring chains so that each chain is hydrogen bonded to each of its six surrounding neighbors.

If this β structure is stretched to a higher degree, the twist in the molecular backbone is partially removed and the hydrogen bonds reform so that there is no longer a hexagonal symmetry in the projection of the amide groups. This results in a monoclinic unit cell which approaches but never reaches the monoclinic cell of Bunn. We refer to this form as the para-crystalline α form, whose unit cell (and density) may vary over a broad range but practically, even in highly crystalline oriented fibers, does not exceed a density of 1.17. We have found a quantitative relationship between density and unit cell parameters of the α(px) phase.

The Bunn structure cannot be achieved in the highly oriented morphology because it requires a fully antiparallel arrangement of molecules. Since the actual arrangement in an oriented fiber is a statistical division between parallel and antiparallel chains, the unit cell adopts the form which results in maximum hydrogen bonding. This necessitates a partially disordered distribution of polar groups. Evidence for this is noted in the degree of imperfection of the 020 reflections characteristic of the polar group spacings. The seventh layer spacing (related to c-c-c zig-zag spacing) is very sharp and well resolved.

The Bunn structure has the smallest unit cell and maximum density. The chains in this form are planar zig-zag and the hydrogen bonds are made between adjacent chains forming a two-dimensional sheet type of structure. In this structure, both the polar groups and the backbone chains are in ordered arrangement. In order to accomplish this, the molecules must be in antiparallel position. We have observed that the Bunn α structure is always found in crystalline bulk polymer which shows spherulitic morphology. It is our belief that the Bunn α form is associated with a chain folded morphology, which automatically must result in a predominantly antiparallel molecular arrangement.

The structure of Brill (4) which had been considered to be at odds with that of Bunn now can be readily explained as an example of one of the para-crystalline α[α(px)] forms.

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ZERO POINTS IN SCHEMES OF RADICAL REACTIVITY

The Q-e scheme was devised to allow monomer reactivity ratios to be predicted from Q,e values assigned to each monomer. Such values were determined by measurement of reactivity ratios for a comparatively small number of monomer pairs, and the value of the approach clearly depends on the possibility of devising a self-consistent set of Q and e values. Such a set has, in fact, been constructed, but recently (1-4) there has been some discussion as to the absolute scale on which the electrical term e should be based. (This is necessarily somewhat arbitrary; at present it is assumed that e = –0.8 for styrene, (5 (a,b)), corresponding to e = 0.0, approximately, for vinyl chloride.) These new considerations are not intended to detract from the empirical value of the Q-e approach, which is not in doubt, but assume significance when it is desired to translate Q,e values into more fundamental terms.

In devising our treatment, described in "Patterns of Radical Reactivity" (6 (a-c)), we sought to eliminate some of the arbitrary features of the Q-e scheme. The obvious importance of the contribution of polar factors to the transition state suggested an approach in which these contributions were expressed in terms of Hammett σ values. We therefore regarded the polymer radicals as substituted ethyl radicals and utilized the σ value(s) of the substituent(s) to express the effect of the latter on the polarization of the transition state. However, in order to do this some standard substrate had to be selected, and for this purpose we chose toluene. The treatment then leads to eq. (1) for the rate coefficient k_s of the reaction of a free radical with a substrate S.

$$\log k_s = \log k_{3,T} + a\sigma + \beta, \tag{1}$$

Here $k_{3,T}$ is the rate coefficient for the transfer reaction of the radical with toluene, and a,β are parameters characteristic of the substrate.

In this treatment <u>any</u> substance may be used as standard, but the values of a,β for any substrate will depend on the particular standard chosen. It is, in fact, easy to show that if a^*,β^* are referred to some substance Z as standard, while a,β are calculated on the toluene standard,

$$\begin{aligned} a^* &= a - a_Z \\ \beta^* &= \beta - \beta_Z \end{aligned} \tag{2}$$

where a_z,β_z are characteristic of Z on the toluene standard. The choice of the standard does not therefore affect the linear form of rela-

tion (1) nor the usefulness of the treatment in predicting radical reactivities; it does, however, determine the nature of the reactivity patterns.

At least in one respect the use of a standard substrate other than a hydrocarbon is basically unsatisfactory. According to any simple treatment of this type a proportionality must exist between the polarity of a radical and that of its conjugate monomer. In the Q-e scheme the two are equated. We have pointed out (6b) that in our treatment σ for a radical and a for its conjugate monomer are related by the simple equation

$$a = -5.3\sigma \tag{3}$$

Such a proportionality naturally demands that if $\sigma = 0$, $a = 0$. It follows that for styrene $a = 0$, and since all the other hydrocarbons examined give the same "pattern," for these also $a = 0$. This situation clearly arises through our use of the Hammett σ, which is zero for hydrogen. In our scheme it would not be logical to use as standard any substrate other than a hydrocarbon, or, perhaps rather more generally, a molecule with $\sigma = 0$. In particular, we could not logically accept Professor Price's standard of $e = -0.8$ for styrene (4) since this would correspond to $a = 1.5$ for the same monomer. Similarly we do not believe e (or Q) values calculated on this scale can be used correctly in conjunction with any quantities evaluated from σ values. Our use of toluene as standard would therefore appear to have only the same degree of arbitrariness as the choice of the zero of σ.

We do not feel that Professor Price's argument (4) relating to the net charge on the double bond can be valid. The treatment of "Patterns" applies equally well to addition and transfer reactions with a common zero in a (5), and it would seem that Price's argument would lead to different zeros.

In any case we are not concerned with the net charge on the unperturbed double bond, but with the contribution of polar forms to the transition state; adherence to Price's concept would lead to the view that when addition to vinyl chloride takes place the transition state is entirely nonpolar, a somewhat unlikely state of affairs. But Price's conclusion that the net charge on the double bond carbons would be very nearly zero is misleading since it disguises the fact that according to his data one carbon will bear a charge -0.56 e.s.u. and the other $+0.62$ e.s.u.; this is much more in keeping with a polar than a nonpolar transition state.

We are grateful to Professor C. C. Price for allowing us to see a copy of his recent communication before publication.

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ANAEROBIC POLYMERIZATION OF VINYL MONOMER-TRIALKYLBORANE MIXTURES

Several investigators (1-4) have reported that polymerization of vinyl monomers by alkyl boranes does not occur in the absence of oxygen. Although this statement is true for vinyl acetate, it is not true for methyl methacrylate, styrene, acrylonitrile, or trifluorochloroethylene. Each of these monomers underwent slow polymerization in the absence of measurable quantities of oxygen.

The polymerization of monomers sealed in ampoules at 10^{-5} mm. Hg was followed by observing the time required for a bubble to rise through the solution. The increase in time required for the bubble to rise was a measure of the viscosity of the solution and hence, a semiquantitative measure of the extent of polymerization. Polymerization of acrylonitrile and trifluorochloroethylene was indicated by the formation of the corresponding polymeric precipitate. All samples were shielded from actinic light.

Detecting trace amounts of oxygen is extremely difficult. One could still argue that even after extraordinary care to remove oxygen (our most sensitive instruments showed its complete absence) a monolayer remained chemisorbed on the surface and that it is available for reaction. If one assumes this to be true, then elementary calculations based on the observed pressure or on an adsorbed monolayer of gas on the glass surface of the ampoule indicate that the maximum possible oxygen available could be 10^{-8} or 10^{-6} millimoles. Thus, the oxygen-triethylborane ratio could be approximately 10^{-8} or 10^{-6}, and the oxygen-monomer ratio could be 10^{-8} or 10^{-10}.

Control samples of neat monomers showed no evidence for polymerization at room temperature over a period of 6 months. Monomers with triethylborane added as initiator, however, showed unmistakable evidence of polymerization after a few days. If the observations are made over a short period of time, the formation of polymer could be missed. Vinyl acetate-triethylborane systems were exceptions, since these showed no increase in viscosity over a 1-yr. period, but polymerized immediately when exposed to air.

The results are summarized in Figure 1. The curves record the change in viscosity of the monomer-triethylborane mixtures, as measured by the time required for a bubble to rise 200 mm. The two curves for methyl methacrylate represent two different samples. Curve A represents a sample of methyl methacrylate purified in a conventional manner, whereas curve B represents a sample purified with meticulous care. Styrene-triethylborane mixtures show appreciable increase in viscosity

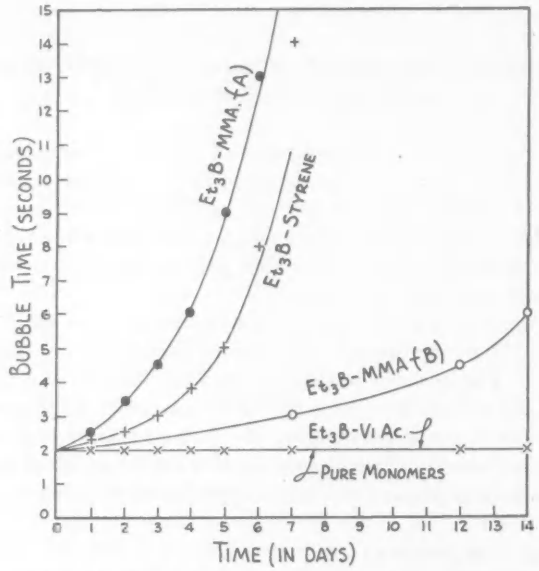

Fig. 1. Viscosity of monomer-Et_3B mixtures.

within 2 days. The curve for vinyl acetate shows no increase in viscosity over a 2-week period; in fact, there was no increase in viscosity over a 1-yr. period.

Yield of precipitated polymer in the ampoules containing acrylonitrile-triethylboranes or trifluorochloroethylene-triethylborane was about 1% after 2 days and 5-10% after 2 weeks.

No visible evidence for polymerization was noted in pure monomers shielded from actinic light over a 6-month period, but extensive polymerization occurred in similar ampoules exposed to the light of the laboratory. Thus, it is evident that monomer-triethylborane mixtures, with the exception of vinylacetate-triethylborane, slowly polymerize under anaerobic conditions.

Experimental

The ampoules, 12 × 250 mm. heavy-walled glass tubing, were attached to a high vacuum line via ground glass joints and evacuated at 10^{-5} and 10^{-6} mm. Hg for 24 hr. at 60°C. Monomer (100 millimoles) and triethylborane (1.0 millimole) were condensed into the ampoules by high vacuum, low temperature transfer techniques (5). Finally, the mixture was frozen with liquid nitrogen, and the ampoule was sealed off under 10^{-5} mm. Hg. Ampoules were stored at room temperature and protected

from actinic light with Eastman Kodagraph film.

The time required for a bubble to rise 200 mm. was measured periodically and these results are plotted in Figure 1. With acrylonitrile and trifluorochloroethylene monomer, there was no significant change in viscosity, since the polymer precipitates from the monomer. The relative amount of precipitate was estimated visually.

Materials

Triethylborane. Commercial triethylborane (Callery Chemical Co.), was distilled from a cylinder into the vacuum line. It was vacuum distilled through traps as −22, −45, and −78°C. The fraction in the −45°C. trap was tensiometrically pure triethylborane.

Methyl Methacrylate. Commercial methyl methacrylate was vacuum distilled at low temperatures from its inhibitor into a recciver containing calcium hydride. This product was then vacuum distilled into another receiver containing calcium hydride, but only the center cut was collected. The purified methyl methacrylate was again vacuum distilled into a receiver containing copper (Mallinkrodt, fine granular), and stored in vacuo at −10°C. and protected from actinic light. The product was again vacuum distilled just before use and the first fraction discarded (curve A, Fig. 1). Extremely pure methyl methacrylate (curve B, Fig. 1) was prepared by repeated distillations (five distillations, using only center cut) from calcium hydride at low temperatures and high vacuum. This product was analyzed by gas chromatography and found to contain only one component.

Acrylonitrile, Styrene, and Vinylacetate. Commercial monomers were distilled at low temperature under high vacuum from calcium sulfate to a storage container which contained copper granules. The distilled product was stored in a refrigerator under an atmosphere of nitrogen. Just prior to use, the container was attached to a vacuum line, the contents frozen with liquid nitrogen, and the container was evacuated. The pure monomer was then distilled from the storage container at low temperature and high vacuum through a column packed with calcium hydride just prior to use.

Trifluorochloroethylene was distilled from a cylinder through a column packed with calcium hydride at low temperature and high vacuum just prior to use.

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GAMMA IRRADIATED CROSSLINKED CELLULOSE

For many years it has been common practice in textile technology to modify the physical properties of cellulose by reaction with bifunctional substances such as formaldehyde. Even though the reaction with formaldehyde was discovered over fifty years ago (1) the exact chemical constitution of the resulting product is not certain. Nevertheless, it is probable that the cellulose chains are linked together by oxymethylene ($-O-CH_2-O-$) bridges (2). Furthermore, due to close packing in the ordered parts of the cellulose, it is most likely that these crosslinkages occur only in the amorphous regions of the polymer.

High energy irradiation of cellulose results in the breakdown of polymer chains (3) and this probably occurs equally in the crystalline and the the amorphous regions (4). However, where crosslinkages have been formed, the fragmented cellulose chains will be held together and be resistant to cellulose solvents. Only in those regions that are free from crosslinkages will dissolution occur and if these are the crystalline regions an amorphous cellulose should result.

Experimental Treatment

Regenerated cellulose in the form of a fabric woven from a viscose staple yarn was reacted with formaldehyde by soaking in an aqueous bath containing 4% formaldehyde and 4% magnesium chloride, squeezing to 100% bath uptake, drying at 80°C. for 1 hr., and finally heating at 150°C. for 12 min. Uncombined formaldehyde was removed by treatment with hot dilute ammonia. This treatment resulted in a fabric containing about 1% combined formaldehyde.

TABLE I

Solubility and Molecular Weights of Celluloses

Formaldehyde treated	Irradiated	% Dissolved	$[\eta]$	D.P. of soluble part	No. average, [a] D.P.
No	No	100	1.56	406	203
No	Yes	100	0.25	64	32
Yes	No	4	–	–	–
Yes	Yes	29	0.73	29	15

[a] Assuming a "most probable" distribution.

Specimens of both untreated fabric and formaldehyde treated material were given a γ-ray dose of 50 Mrads in the Harwell Irradiation Pond. No attempts were made to exclude air or moisture.

Solubility and Viscosity

Irradiated and unirradiated samples of both crosslinked and untreated cellulose were shaken for half an hour with 25 cc. of cuprammonium hydroxide solution. The untreated celluloses dissolved completely, the crosslinked unirradiated one had the same form before and after shaking but the crosslinked irradiated fabric disintegrated into a mass of loose individual filaments. After filtration undissolved material was washed with water, dilute acetic acid, and a large volume of distilled water before drying and weighing. The viscosity of the filtrate was used to calculate the intrinsic viscosity using the equation (ref. (5))

$$\log_{10} (\eta_{sp}/c) = \log_{10} [\eta] + 0.13\ c[\eta]$$

and the degree of polymerization was calculated using a Staudinger constant of 260 (6). The results obtained are shown in Table I.

X-ray measurements show about 40% of regenerated cellulose to be crystalline and deuterium exchange experiments (7) have suggested that about 20 to 25% is not accessible to water molecules. Now it is quite likely that this material will also be inaccessible to the larger formaldehyde molecules and therefore free from combined formaldehyde. For the case where the entire 1% of combined formaldehyde exists as single oxymethylene crosslinkages, the accessible parts of the structure will have on the average about 7 anhydroglucose units between each crosslink. With the chain breaking rate of roughly 1 in 35 (calculated from the first two entries of the Table I), it is unlikely that very much of the crosslinked structure will be rendered sufficiently small to be soluble.

In one regenerated cellulose Sharples (8) has shown that the mean

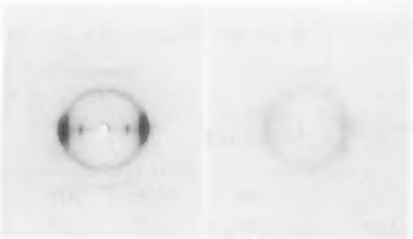

Fig. 1. X-ray fiber diagrams of crosslinked irradiated cellulose. (Left), before extraction with cuprammonium hydroxide; (right), after extraction with cuprammonium hydroxide.

crystallite length is about 30 units, and provided the radiolysis rates are similar in the crystalline and amorphous regions (4), it is probable that many sections of polymer chain in the crystallites will be broken out and rendered soluble. The extra portion of cellulose rendered soluble by the irradiation is about 25% and is comparable with the amount of material inaccessible to water. The figure of 15 units given in Table I for the mean length of the dissolved cellulose is smaller than the chain length of the untreated cellulose after irradiation under similar conditions and is also smaller than the 30 units quoted for the crystallite length. This is due to the improbability of breaking out each portion of cellulose chain by neat scission at the ends of the crystallites compared with breakage at points inside the crystallites. This is concordant with the concept of preferential solubility of the crystalline portions.

X-Ray Diffraction

If, as is suggested by the above arguments, it is mainly the crystalline portions of the cellulose that are rendered soluble by the irradiation this should be shown by the intensity of the crystalline arcs in the x-ray diffraction pattern. X-ray fiber diagrams of the untreated cellulose, formaldehyde treated cellulose, and the same two celluloses after irradiation were obtained. No appreciable change was observed in the diffraction pattern or intensity and the photograph taken of the formaldehyde treated and irradiated specimen shown on the left in Figure 1 is typical of the others. After extraction with cuprammonium hydroxide however, the very different picture on the right resulted. In agreement with our hypothesis that most of the crystalline material has been removed this latter photograph has only diffuse and rather faint diffraction arcs.

Trapped Radicals

We have recently shown by the irradiation of regenerated celluloses having different crystalline/amorphous ratios that the stable radicals formed in cellulose by high energy radiation are located in the highly ordered or crystalline portions of the material. An electron spin resonance spectrum of the irradiated crosslinked cellulose gave, at a very rough estimate, about one stable radical for every 10^4 to 10^5 glucose units. After extraction with cuprammonium hydroxide all the radicals were removed, an observation which is again in accord with the selective removal of the ordered regions of the cellulose. Attention has been drawn elsewhere (9) to the symmetrical nature of the spectrum obtained in this cellulose which is in contrast with the previously published (10) unsymmetrical ones.

Water Sorption

The compact nature of the ordered regions of the cellulose renders these inaccessible to water and so decreases the equilibrium water uptake at any given vapor pressure. The removal of these regions by any method should therefore increase the quantity of water sorbed per unit weight of solid. The equilibrium water content at 70% relative humidity has been determined for both the specimens whose x-ray diffraction diagrams are shown in Figure 1. The extracted low crystallinity material had a water vapor regain of 19.6% compared with the value of 15.6% for the unextracted cellulose. In the absence of other changes a difference in water uptake of this size would be expected for a loss of only 20% of crystalline material on extraction. The actual loss which is greater than this may therefore consist partly of noncrystalline cellulose. Alternatively, a rearrangement of the polymer chains could occur after extraction leading to a lower water sorptive capacity.

It appears from these experiments that the formaldehyde crosslinking reaction occurs in the amorphous regions of the cellulose only and holds these together after irradiation when the crystalline portions are dissolved. The preferential attack on the crystalline portions is the reverse of the effect obtained by other means (with hydrolytic reagents for instance).

The properties of the disordered crosslinked cellulose remaining merit further investigation.

Thanks are due to Mr. L. Brown of Courtaulds, Ltd., Coventry, for the x-ray diagrams, to Dr. J. C. Ward for the ESR spectra and to Dr. Roberts of A.E.R.E., who made arrangements for the irradiations.

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COMPARISON OF SOLUBILITY DATA FOR IRRADIATED POLYPROPYLENE

In three recent publications gel fractions as a function of dose have been given for polypropylene irradiated in a Co^{60} γ-ray source (1), in a Van de Graaf electron generator (2), and in a nuclear reactor (3). In two of these publications (1,2) it was shown that the data gave linear $S + S^{1/2}$ versus $1/r$ plots in accord with the equation of Charlesby and Pinner (4), where S is the fraction of polymer soluble in a suitable solvent at a given dose, r. It was believed of interest to analyze the data for the reactor irradiated samples in a like manner and make a comparison of the data obtained in all three studies; this is done in Figure 1.

It is seen in the figure that when the solubility function, $S + S^{1/2}$ is plotted against γ-ray dose, instead of total energy deposition (γ-ray dose/total dose = 0.565), for the reactor irradiated samples (3), close agreement between the data for isotactic annealed film specimens and those for γ-ray irradiated isotactic film is found for $1/r$ values of about 0.005 to 0.04 $Mrads^{-1}$. A line through the points in this range (line 3) has essentially the same intercept (0.75) but a somewhat lower slope than line 2. It should be pointed out that since the γ-ray and reactor irradiated samples were obtained from the same supplier (Hercules Powder Co.), their physical properties are probably similar, if not the same.

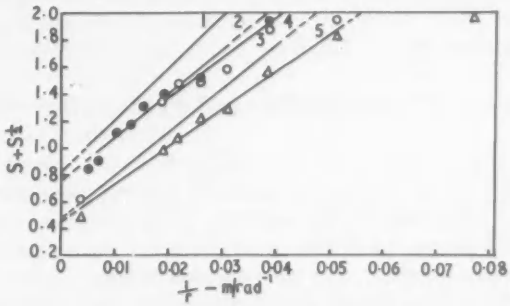

Fig. 1. Solubility of polypropylene as a function of irradiation dose. Data of Salovey and Dammont (2) for atactic polymer, line 1. Data of Schnabel and Dole (1): for isotactic film, line 2; for atactic polymer, line 4. Data of Chappell, Sauer, and Woodward (3): annealed isotactic film irradiated at 100 kilowatt power (r refers to γ-ray dose), (●) and line 3; same, but irradiated at 200 kw. power, (○); quenched isotactic film irradiated at 200 kw. power, (Δ) and line 5. (Dotted portions of lines are extrapolations).

It can also be seen that the data for the reactor irradiated quenched isotactic film fall close to, but below the line for γ-ray irradiated atactic material, yielding an intercept of 0.43. However, decided differences occur for electron and γ-ray irradiated atactic polymer with the intercepts varying by a factor of two.

Extrapolation of lines 3 and 5 to the maximum value of $S^{3/2}$ would indicate that for 1/r greater than 0.041 and 0.055 Mrads^{-1} the reactor irradiated annealed and reactor irradiated quenched samples, respectively, should be completely soluble. As indicated in the figure, small amounts ($\sim$ 3%) of gel were found up to 1/r values of 0.077 Mrads^{-1}, but due to the large errors inherent in such small values, this discrepancy may not be a real one. It is also seen that the point at the lowest 1/r value for the reactor irradiated annealed sample falls considerable below line 3, being closer to line 5 for the reactor irradiated quenched film.

A log 1/r versus log S plot for the reactor irradiated quenched film was constructed and the straight line through all the points yielded a slope of 1.4 in close agreement with the 1.5 value assumed in Figure 1. For the reactor irradiated annealed film a line drawn through all the points exhibited curvature; ignoring the value at the highest dose, gave a straight line with a slope of 1.7.

The expression of Charlesby and Pinner (4) for a polymer having the most probable molecular weight distribution ($\bar{M}_w/\bar{M}_n = 2$) in which crosslinking and scission are occurring relates the solubility, the dose, the number of main chain scissions per 100 ev. of energy absorbed, G(S), the number of intermolecular crosslinks formed per 100 ev. of energy absorbed, G(X), the weight average molecular weight, $\bar{M}_w$, and Avogadro's number, N_A, as follows:

$$S + S^{1/2} = G(S)/2G(X) + [100\, N_A/r\bar{M}_w G(X)]$$

As pointed out previously (1,2), it is surprising that a linear $S + S^{1/2}$ versus 1/r plot should be obtained at all for polypropylene due to the large M_w/M_n value found for this polymer. Some deviations from this equation at the lowest and highest dosages were indicated above for the reactor irradiated samples. The most serious of these is the one found at the lowest 1/r value for the annealed isotactic film. Since there is little data available, further studies at doses greater than 20 Mrads are necessary to clarify this point. A further indication that this equation is of doubtful validity for annealed isotactic polypropylene comes from the use of it to obtain a comparison of the amounts of crosslinking and scission which occur for reactor irradiated, annealed, and quenched samples. Since these two sets of samples have the same initial $\bar{M}_w$ and the slopes of their $S + S^{1/2}$ versus 1/r plots are about the same, it would indicate that the lower intercept (by a factor of two) for the

quenched samples is due to a lower G(S) value with G(X) remaining essentially constant. This is a most surprising result and is in contrast to the conclusion of Schnabel and Dole (1) that atactic and isotactic polypropylene have the same G(S) value.

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POLYMER LETTERS VOL. 1, PP. 625-627 (1963)

POLYSULFONES OF NORBORNADIENE

The reaction of aqueous ethanol solutions containing olefins with sulfur dioxide has been reported to yield sulfones and polysulfones in the presence of copper(II) salts (1). Recently in this laboratory (2) we have investigated this reaction system as a possible route to the preparation of crystalline copper(I)-olefin compounds and have realized satisfactory yields of the olefin complexes containing cyclic olefins. An attempt to extend this reaction to the preparation of a nickel-olefin compound containing norbornadiene by the substitution of nickel(II) chloride hexahydrate for hydrated copper(II) chloride resulted in the formation of a polysulfone of norbornadiene. The reaction of vinylcyclohexene and 1,5-cyclooctadiene under similar conditions also yielded polysulfones but these products have not been investigated in detail.

In order to evaluate the catalytic activity of nickel chloride in this system a series of reactions were carried out in which ethanolic solutions of freshly distilled norbornadiene were treated with sulfur dioxide in the presence of (a) no added catalyst, (b) nickel(II) chloride-hexahydrate, and (c) hydrogen peroxide.

Similar products were obtained from the reactions employing no added catalyst or nickel(II) chloride. The only difference noted in the first two reactions was the slightly increased rate of polymer formation in the presence of nickel(II) chloride although the same quantity of product (nearly quantitative yield) was obtained after 48 hr. This polymer, I, was insoluble in common solvents, however, it dispersed and appeared to swell in methylene chloride, N,N-dimethylformamide and dimethylsulfoxide.

In the reactions employing hydrogen peroxide as the catalyst the formation of the polysulfone occurred immediately upon the addition of sulfur dioxide to the reaction mixture. The product of this reaction, polymer II, was soluble in N,N-dimethylformamide and dimethylsulfoxide. The inherent viscosity of polymer II was determined in N,N-dimethylformamide and dimethylsulfoxide utilizing an Ostwald viscometer. Values for $\eta_{inh.}$ of 0.93 and 1.02 were obtained, respectively, at a concentration of 0.5 g./100 ml. of solvent at 25°C. These values are comparable to those reported for the polysulfones of 1,5-cyclooctadiene (3) and 1,5-hexadiene (4).

The carbon, hydrogen, and sulfur analyses indicated a 1:1 ratio of norbornadiene to sulfur dioxide in both polymers. Analyses were somewhat low possibly due to entrapment of solvent in the polymer network which could not be removed by vacuum drying at moderate temperatures.

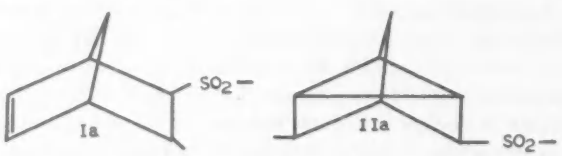
X-ray powder patterns of polymer I contained two rather diffuse lines

indicating a definite degree of crystallinity whereas polymer II, was completely amorphous. The x-ray diffraction data are consistent with the observed solubilities of polymers I and II.

The infrared spectra of polymers I and II are similar except for the appearance of two medium intensity bands at 1222 $cm.^{-1}$ and 705 $cm.^{-1}$ in polymer II. The spectra of both polymers contain the diagnostic (5,6) nortricyclene bands at 3070 $cm.^{-1}$, 1040 $cm.^{-1}$, and 815 $cm.^{-1}$ and in addition the absorption bands at 1580 $cm.^{-1}$ and 720 $cm.^{-1}$ indicate the presence of norborene units (7). The absorption bands at 1300 $cm.^{-1}$ and 1128 $cm.^{-1}$ ($-SO_2-$) are not significantly different from similar absorption bands found in pentamethylene sulfone (4).

The most notable feature of the spectra is the difference in the intensities of the bands associated with the nortricyclene and norborene configurations. In polymer I the absorption bands associated with the norborene unit are of higher intensity whereas those associated with the nortricyclene system predominate in polymer II. The higher proportion of free double bonds (norborene units) in polymer I increases the potential for crosslinking in this material which may also account for its lower solubility.

In view of the above evidence it appears that both polymers I and II contain a mixture of the monomer units Ia and IIa with Ia predominating in polymer I and IIa in polymer II.



Experimental

Polymer Preparation. Sulfur dioxide was added to a solution containing 0.1 mole of freshly distilled norbornadiene (b.p. 88-89°C.) in 30 ml. of ethanol until the precipitation of product was noted. The reaction mixture was stored at room temperature for 48 hr. and the product separated by filtering. The crude material, which had been washed with ethanol and dried in air, was dispersed in methylene chloride and reprecipitated in methanol. Analysis and spectra were determined on samples which had been vacuum dried at 78°C. over phosphorus(V) oxide and paraffin. The analyses for the various products are compiled in Table I. The yields from each reaction were nearly quantitative.

TABLE I

Analysis of Polysulfones of Norbornadiene [a]

Reaction	Catalyst	Found		
		C	H	S
a	None	51.46	5.21	18.7
b	0.01 mole of $NiCl_2 \cdot 6H_2O$	51.31	5.01	19.2
c	0.0075 mole of H_2O_2	51.63	5.64	18.8

[a] Calcd. for $(C_7H_8SO_2)_x$: C, 53.83; H, 5.16; S, 20.53.

We wish to express our appreciation to Dr. W. J. Miller and Mr. J. Hegenbarth for assistance in obtaining the viscosity and x-ray powder patterns and to Dr. J. K. Stille for helpful comments and suggestions. This investigation was supported by U. S. Army Research Office, Durham, Grant DA–ARO(D)–31–124–G26.

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POLYMORPHISM IN POLY-p-ETHYLENE OXYBENZOATE

The x-ray patterns of drawn fibers of poly-p-ethylene oxybenzoate, $-(C_6H_4 \cdot CO \cdot O \cdot CH_2 \cdot CH_2 \cdot O-)_n$ (PEOB), have been the subject of at least two publications (1,2). Korematsu and Kuriyama (2) have pointed out that the identity period of PEOB was 15.5 A., whereas the value calculated from the molecular configuration was 19.6 A. They have also noticed the diffraction spots arising from the identity period of about 19 A. in the x-ray pattern of PEOB fiber which is highly drawn and annealed without being allowed to contract. The purpose of this short report is to show the conversion of the modified crystalline phases of PEOB.

X-ray diffraction patterns were taken on flat plate film at a sample-to-film distance of 50.0 mm. with nickel-filtered copper K_α radiation. When an undrawn yarn of noncrystalline phase of PEOB is drawn, an oriented, noncrystalline phase is obtained (Fig. 1). An oriented, crystalline phase is produced by annealing the oriented, noncrystalline specimen at 170°C. for 2 hr. with being allowed to contract (Fig. 2). This crystalline phase is very stable for annealing and it is tentatively named α-form. This α-form shows the identity period of 15.7 A. Another crystal-

Fig. 1. X-ray pattern given by untreated yarn of PEOB drawn 4.5 × at 60°C. Fiber axis vertical.

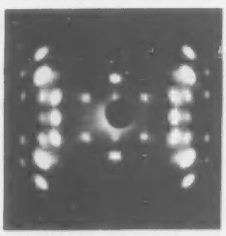

Fig. 2. X-ray pattern given by drawn yarn of PEOB annealed at 170°C. for 2 hr. and allowed to contract, α-form.

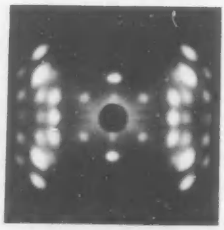

Fig. 3. X-ray pattern given by PEOB yarn of α-form annealed at 150°C. for 30 min. and not allowed to contract, β-form.

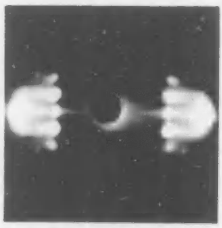

Fig. 4. X-ray pattern given by PEOB yarn of α-form annealed at 150°C. for 30 min. and allowed to contract, γ-form.

line phase is obtained by stretching the specimen of α-form about 30% from the original length at a room temperature and annealing at 150°C. for 30 min. (Fig. 3). This new crystalline phase is temporarily named β-form. The identity period of the β-form is almost the same as that of the α-form. When the specimen of β-form is annealed at 170°C. for 30 min. and allowed to contract, the β-form is converted into the α-form. However, if the same annealing is done without allowing contraction, another phase is obtained (Fig. 4). This new crystalline phase tentatively named γ-form. This γ-form shows two identity periods of 15.7 A. and 19.1 A. The γ-form is also converted into the α-form by annealing at 170°C. for 30 min. and allowed to contract. The γ-form is directly produced by annealing the oriented, noncrystalline specimen (Fig. 1) at 140°C. for 3 sec. and not allowing contraction. Thus, it should be considered that shortened and inclined chains to the fiber axis are contained in the α- and β-forms, and fully-extended chains co-exist in the γ-form.

The detailed structures of these crystalline forms of PEOB are being studied and a complete paper is in preparation.

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PROTON MAGNETIC RESONANCE SPECTRA OF POLY-α-METHYLSTYRENE

In recent publications (1-3) we have reported that α-methylstyrene is polymerizable with Ziegler-type catalysts, and that poly-α-methylstyrene having different degrees of stereoregularity (as deduced from measurements of several properties) can be obtained by changing the polymerization conditions, especially the type of catalyst. Regardless of the polymerization conditions, no poly-α-methylstyrene crystallizes when given the usual treatment to encourage crystallization. Moreover, estimates of the degree of stereoregularity from glass transition temperatures, infrared absorption spectra, and x-ray scattering intensity curves

TABLE I

Polymerization Conditions and Intrinsic Viscosities of Poly-α-Methylstyrene [a]

Catalyst	Sample No.	Catalyst aging condition	Polymerization temperature, °C.	$[\eta]$, dl./g.
$AlEt_3$–$TiCl_4$	Z-14-835 [b]	0°C., 20 min.	−78	1.263
	Z-14-1072	−78°C., 40 min.	−78	0.454
$BF_3 \cdot OEt_2$	B-16 [b]	–	−78	0.988
	BL-13	–	−60	0.932
	B-100-11	–	0	
$TiCl_4$	Z-14-796 [b]	–	−78	0.575
K	KM-3-1 [c]	–	20	1.118
Na	NM-1-1 [c]	–	20	0.527
$AlEt_2Cl$	Z-14-1082 [b]	–	−78	1.027
$AlEtCl_2$	Z-18-1 [b]	–	0	0.032
	Z-18-3	–	−30	0.433
	Z-18-5	–	−78	0.816
BuLi	LM-3-4 [d]	–	20	0.174

[a] Details of polymerization conditions have been shown in previous papers (1-3).

[b] Toluene and n-hexane mixture used as solvent.

[c] Bulk polymerization.

[d] Tetrahydrofuran used as solvent.

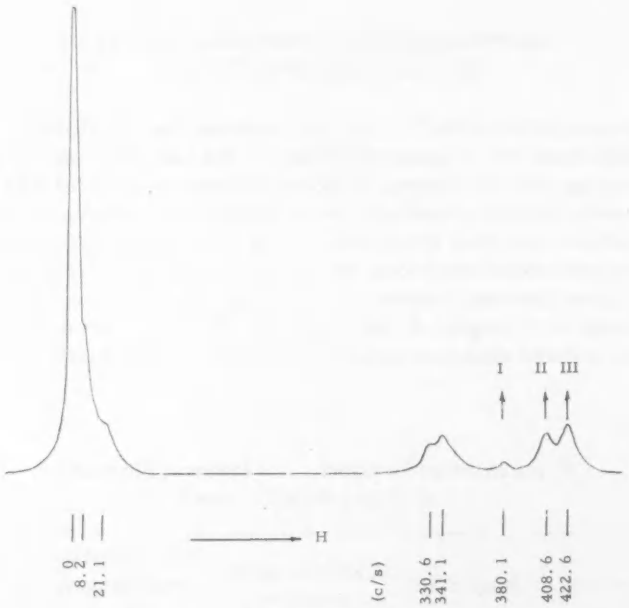

Fig. 1. Nuclear magnetic resonance spectra of 10% poly-α-methylstyrene solution in chloroform. Sample NM-1-1, 80°C.

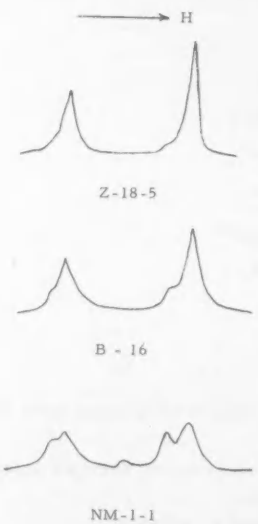

Fig. 2. Signals of methylene chain protons and α-methyl group protons.

TABLE II

Chemical Shifts (Based on $CHCl_3$)

Sample No.	$-CH_2-$		$-CH_3$		
	I (C/S)	II (C/S)	I (C/S)	II (C/S)	III (C/S)
NM-1-1	330.1	340.6	380.1	407.9	422.0
B-16	330.1	340.6	–	409.1	422.3
B-16	330.4	340.6	–	408.5	423.2
Z-14-796	331.9	342.8	–	408.9	422.7

of powder samples agreed only qualitatively.

Several other workers (4-6) have recently claimed that the degree of local regularity of poly(methyl methacrylate) can be determined quantitatively by analysis of the signals attributed to the α-methyl protons in the NMR spectra.

Poly-α-methylstyrene has phenyl ring sidechains, and these phenyl rings show diamagnetic anisotropy. One can therefore expect to be able to deduce the degree of local regularity of poly-α-methylstyrene from its NMR spectra. In general a proton occupying a position on or near the sixfold axis of a benzene ring should be shielded by the interatomic diamagnetic effect; this would cause the proton signals to shift in the direction of higher magnetic field, because, in a magnetic field the π-electrons of a phenyl ring produce ring currents and thus an added local magnetic field (7).

We wish to report the NMR spectra of poly-α-methylstyrene obtained with Ziegler-type catalysts, cationic catalysts, and anionic catalysts and to discuss the changes of stereoregularity of poly-α-methylstyrene resulting from differences in the polymerization conditions. Brownstein and co-workers (8) have also made NMR studies of poly-α-methylstyrene and discussed them from the same point of view.

Samples

The polymerization conditions of the samples used are summarized in Table I. Details have been presented in previous papers (1,2).

Results and Discussion

NMR spectra of 10% poly-α-methylstyrene solutions in chloroform have been measured at 80°C., using Varian Associates Model DP-60. Typical spectra are shown in Figure 1. Tetramethylsilane was not available. Therefore, the locations of all peaks are indicated by their chemical shifts expressed in cycles per second from the peak of the proton of

TABLE III

Stereoregularity of Polymers

Sample No.	Catalyst	Polymerization temperature, °C.	I	II	III
Z-18-5	$AlEtCl_2$	−78	–	8	92
Z-18-3	$AlEtCl_2$	−30	6	13	81
Z-18-1	$AlEtCl_2$	0	5	15	80
B-16	$BF_3 \cdot OEt_2$	−78	–	13	87
BL-13	$BF_3 \cdot OEt_2$	−60	–	14	86
B-100-11	$BF_3 \cdot OEt_2$	0	1	16	83
Z-14-796	$TiCl_4$	−78	3	17	80
Z-14-835	$AlEt_3$–$TiCl_4$	−78	4	24	72
Z-14-1072	$AlEt_3$–$TiCl_4$	−78	6	27	67
Z-14-1082	$AlEt_2Cl$	−78	1	29	70
KM-3-1	K	20	6	31	63
NM-1-1	Na	20	9	33	58
LM-3-4	BuLi	20	5	37	58

chloroform. Two signals at 8.2 and 21.1 c.p.s. are ascribed to the protons of the rings in the polymer. The signals at 330.6 and 341.1 c.p.s. are due to the protons of the methylene chain groups. The remaining three signals, at 380.1, 408.6 and 422.6 c.p.s. are due to the protons of the α-methyl groups. These assignments are almost the same as those given by Brownstein et al. (8), although they did not observe the splitting of methylene proton peaks. The changes of the spectra resulting from differences in the polymerization catalysts can be seen roughly from Figure 2. Note that the shapes of the signals ascribed to methylene protons are similar to those of the signals at 408.6 and 422.6 c.p.s. in each spectrum. The position of each signal, defined as the chemical shift from the signal of the chloroform proton, is always constant and independent of the shapes of the signals, as shown in Table II. This shows that the molecular chains of poly-α-methylstyrene obtained with various catalysts consist of the same local structural units, independent of the polymerization conditions, and that the intensity changes of the signals are due to differences of stereospecificity in the polymers.

The three signals assigned to α-methyl protons probably correspond to different local structural units: isotactic, heterotactic, and syndiotactic, as postulated by Bovey and Tiers (4) in the case of PMMA. The relative areas of the three signals, calculated in the same manner as in the case of PMMA, are shown in Table III. The relative areas of the signal at 422.6 c.p.s., for polymers produced with the different catalysts,

are as follows:

$$AlEtCl_2 \geq BF_3 \cdot OEt_2 > TiCl_4 > AlEt_3\text{–}TiCl_4$$

$$\geq AlEt_2Cl > K \approx Na \approx BuLi$$

This order is similar to that obtained for the stereoregularity of polymers resulting from different catalysts as deduced from measurements of glass transition temperatures, infrared absorption spectra, and x-ray scattering intensity curves, except that the place of $AlEt_3$–$TiCl_4$ catalyst in the order obtained here is different from that in the order

$$AlEt_3\text{–}TiCl_4 \geq BF_3 \cdot OEt_2 \geq TiCl_4 > K \approx Na$$

obtained from the other measurements. The reason for this discrepancy is uncertain. It may perhaps be related to the stereoregular sequence length.

The following conclusions may be drawn from a consideration of Table III. The polymers obtained cationically are mostly stereoregular. Anionic catalysts give a random structure. The Ziegler catalysts, which we consider to induce cationic polymerization, seem to give greater randomness of structure than the usual cationic catalysts. Although most stereoregular polymers have been obtained by $AlEtCl_2$ at low temperatures (–78°C.), the polymer obtained using $AlEt_2Cl$, which has been considered to induce cationic polymerization as does $AlEtCl_2$, has a more random structure – like the polymers obtained by Ziegler catalysts or anionic catalysts. It is especially interesting to find entirely different degrees of stereoregularity in the polymer produced by different kinds of cationic catalyst with the other polymerization conditions the same. The effects of polymerization temperature on the molecular structure were also examined for products obtained using the cationic catalysts $AlEtCl_2$ and $BF_3 \cdot OEt_2$. Although the effect of differences in temperature is not large in comparison with the effects of differences in the kind of catalyst, a lower temperature is found to favor a more regular structure.

It is very difficult to identify the structures responsible for the three signals of α-methyl from the NMR data alone. Brownstein and his coworkers (8) have related the three signals of α-methyl in increasing order of the magnetic field, to isotactic, heterotactic, and syndiotactic structures, respectively. These assignments are the same as for PMMA. As they have mentioned, it is impossible to make a model of a chain having more than two or three monomer units using Fisher atomic models, because of the steric hindrance between bulky groups such as α-phenyl and α-methyl. However, it is necessary to consider at least three monomer units of a chain in assigning the three signals attributed

to α-methyl. The positions and the directions of the phenyl groups are very important, in determining the effects of diamagnetic shielding of their π-electrons. Therefore, unless we can obtain, from x-ray data or otherwise, detailed knowledge of the structure, the three signals of α-methyl cannot be definitely assigned. According to the assignments of Brownstein et al. (8), poly-α-methylstyrene obtained with cationic catalysts at low temperature (−78°C.) is largely syndiotactic, while polyvinyl ether obtained with a Ziegler catalyst or cationic catalysts at low temperature is isotactic. Also polybenzofuran obtained with the aid of $AlEt_2Cl$, using an optically active substance at low temperatures, is optically active and presumably isotactic (9). Until now, no syndiotactic products have been reported as obtained by a cationic catalyst in nonpolar solvent. However, we have obtained an x-ray fiber diagram of poly-α-methyl styrene prepared with $AlEt_3$–$TiCl_4$ catalyst at −78°C., by heat stretching under special conditions. This x-ray fiber diagram shows a fiber identity period of 6.6 A. with a rhombohedral structure. The crystalline part presumably has an isotactic structure.

Splitting of the methylene proton signals into two components has been clearly observed. The ratio of the intensities of these components is roughly proportional to that of the signals at 408.6 and 422.6 c.p.s. This means that the splitting has a different origin from that in the case of PMMA, where the signals of methylene protons split purely as a result of spin-spin interactions. It seems probable, therefore, that other assignments should be given to the three signals attributed to α-methyl, and that the signal of 422.6 c.p.s. is due to isotactic configurations. Further x-ray and NMR studies are required, however, before definite conclusions can be reached in this regard.

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TRANSIENT OSMOTIC EFFECTS

The general trend toward more rapid analysis has been reflected in developments in osmometry. Increasing use of the dynamic methods has prepared the way for more automatic versions of osmometric procedure. The increasing speed of analysis now makes it possible to evaluate such influences as the pressure contribution by rapidly permeating solute, which formerly often were too fleeting even to be observed.

It had been observed, during use of the dynamic method (1) for osmotic pressure determination, that sometimes transient osmotic pressures were developed which took up to one half hour or more to disappear. After eliminating suspected effects such as membrane ballooning, temperature transients, and others, the observation was made that such effects often took place when the two half-cells of the osmometer were filled with solvent from different batches. It was soon realized that impurities of low molecular weight, more concentrated in one batch of solvent than in the other, gave rise to these transient osmotic pressures.

For the present experiments, use was made of an automatic osmometer (2), in which a servo mechanism imposes a hydrostatic pressure on the solvent half-cell such that at any time the volume flow across the osmometer membrane tends toward zero. Under this condition the applied hydrostatic pressure, which is read from a dial or from the graphical recording, equals the osmotic pressure of the solution. In the experimental procedure, a blank- or zero-line is first established with solvent and sample chambers filled with identical solvent. In the absence of permeating solute, the solvent is allowed to remain in the solvent chamber, but if the sample contains membrane-permeating solute, the solvent chamber must be flushed every time. This is done by injecting

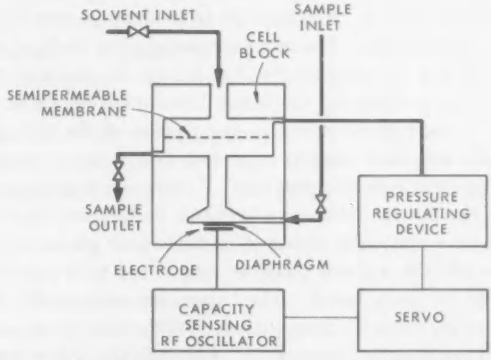

Fig. 1. Schematic diagram of automatic osmometer.

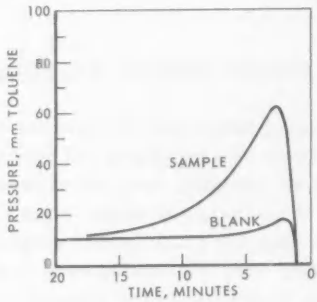

Fig. 2. Transient osmotic pressure due to impurities in toluene. Sample: reagent grade toluene measured against redistilled toluene (cf. text); retraced from strip chart recording.

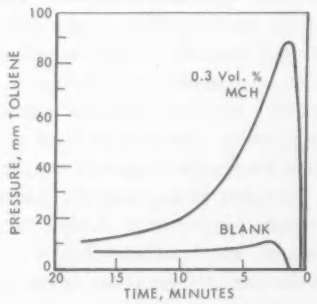

Fig. 3. Transient osmotic pressure due to 0.3 vol.-% methylcyclohexane; retraced from strip-chart recording.

fresh solvent into the solvent system through a petcock on the front panel of the instrument. In our experiments, gel cellophane 600 served as the osmometer membrane. Reagent grade toluene (Baker and Adamson) was used as the solvent. The measurements were made at 34°C. The operation of filling the sample chamber lasted 30 sec. and followed a pattern such that reasonably flat blank lines were obtained (Fig. 2 and 3; time zero in the figures refers to completion of the filling procedure). This operation was then exactly repeated with solution instead of solvent. The apparent osmotic pressure, P, due to compounds dissolved in toluene is given by the difference between sample and blank curves. Figure 2 shows a transient obtained with reagent grade toluene as "sample," while the solvent chamber was filled with carefully redistilled toluene of the same batch. The impurities responsible for the transient were not identified. Comparison of refractive index suggested the presence of nonaromatic compounds. Accordingly, a concentration of 0.3 vol.-% of methylcyclohexane, e.g., gave an osmotic pressure of sev-

eral centimeters of toluene, which declined as the solute diffused through the membrane. A plot of log P versus time gave straight lines after a time interval of about 2 to 3 min. and could readily be extrapolated to zero time. The extrapolated pressures were found to be proportional to concentration; but due to the Staverman effect (3) they represent only a fraction of the theoretical pressure calculated by van't Hoff's relationship.

Effects of this kind may give rise to unduly long equilibration times in molecular weight determinations of polymers by rapid osmometry depending on the diffusion rates of the low molecular weight compounds. If caused by impurities in the solvent they can be avoided simply by filling the solvent compartment of the osmometer with the same solvent as used for preparing the sample solutions.

The effect of a variety of compounds is presently being studied in our laboratory with the aim of elucidating some aspects of membrane behavior.

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THE INFRARED SPECTRUM OF ETHYLENE-PROPYLENE COPOLYMERS AND THE DETERMINATION OF PROPYLENE CONTENT

Infrared spectroscopic methods for the determination of propylene content in ethylene-propylene copolymers have been reported (1,2). These determinations were concerned with high (30-70 mole %) propylene content. In work reported recently, Smith, Stoffer, and Hannan (3) presented a method for the determination of low (0-10 mole %) propylene content. Their method consists of measuring the 8.7 μ (1149 cm.$^{-1}$) methyl wagging frequency and correlating this to propylene content obtained from radiochemical analysis of polymers made with C^{14} labeled propylene. They also show a band they report as 10.37 μ (965 cm.$^{-1}$) which is claimed to be due to trans unsaturation. As it is rather inconceivable that they could produce a polymer of ethylene and propylene with trans unsaturation only, this latter assignment must be incorrect. From the positions of the bands they report as 8.7 and 10.37 μ, it appears they are actually the 1154 and the 974 cm.$^{-1}$ bands of amorphous polypropylene. As the infrared spectrum of block copolymers is simply the superposition of the spectra of the homopolymers, it is apparent their materials are block copolymers.

Phillips and Carrick (4) report the preparation of a linear random copolymer of ethylene and propylene. They do not report the presence of a band at 1154 cm.$^{-1}$ but instead use a compensation technique on the 1378 cm.$^{-1}$ methyl band to determine propylene content. Furthermore, in the infrared spectrum of nonstereospecific polypropylene prepared by Liang and Watt (5), no band is seen at 1154 cm.$^{-1}$ even though large numbers of pendant methyl groups must be present.

In a paper reporting the free-radical copolymerization of ethylene and propylene (6), it was reported that about 4% of the propylene acts as a chain transfer agent by transfer of an alpha-hydrogen to the active site at the end of a growing polymer chain and propagating a new chain from the propylene radical formed. The other 96% of the propylene is copolymerized into the molecule. Investigations of this type of copolymer show no absorption bands at 1154 and 974 cm.$^{-1}$ thus indicating these materials to be random copolymers. In random copolymers of ethylene and propylene, the presence of the propylene can be detected by the functional groups produced. In free-radical initiated copolymers, the vinyl content is a measure of the amount of propylene used as a chain transfer agent and the enhancement of the methyl absorption at 1378 cm.$^{-1}$ is a measure of the amount of propylene entering the molecule as a comonomer. As there are large numbers of pendant methyl groups pro-

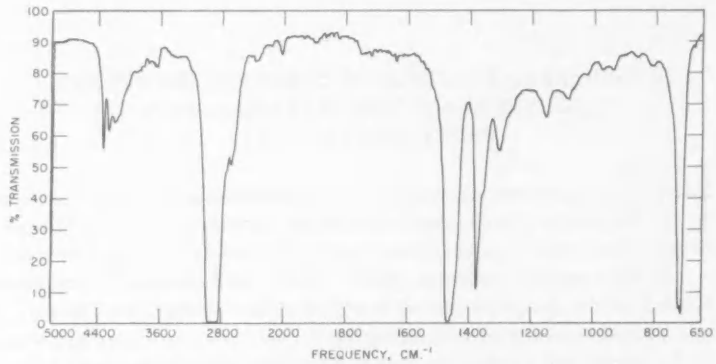

Fig. 1. Block copolymer of ethylene and propylene containing 4.8% propylene.

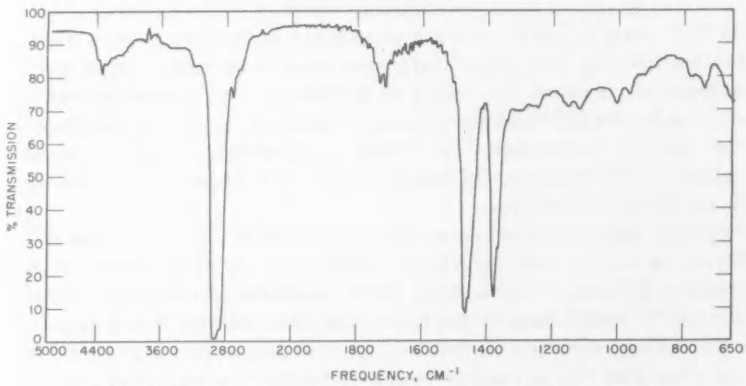

Fig. 2. Nonstereospecific polypropylene by the method of Liang and Watt (5).

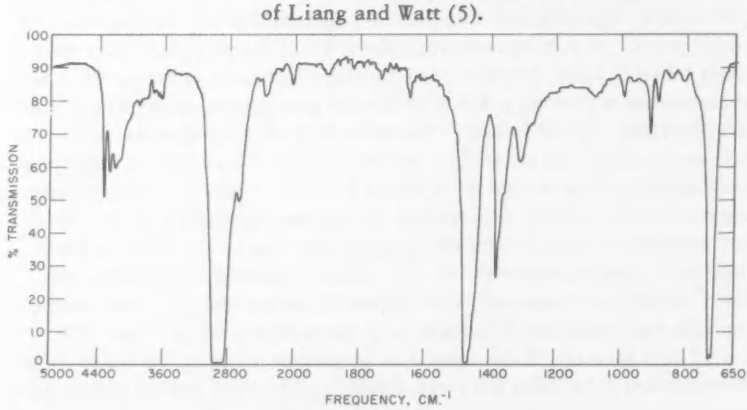

Fig. 3. Random copolymer of ethylene and propylene containing 6.4% propylene.

duced in these free-radical initiated copolymers and no band is seen at 1154 cm.$^{-1}$, then the inferred assignment of this band to a wagging mode of pendant methyl groups per se must be incorrect.

The assignment of the band at 1154 cm.$^{-1}$ to a wagging mode of the pendant methyl groups was made from a study of deuterated polypropylenes (7). However, in the manner in which the assignment was made, it was specifically for the wagging motion of the pendant methyl groups of polypropylene, and not necessarily for any other type. Therefore, the lack of a band at 1154 cm.$^{-1}$ in copolymer spectra could lead to the conclusion that there are no pendant methyl groups present.

It is the contention of the author that the 1154 cm.$^{-1}$ band is a function of polypropylene segments, either as blocks in a copolymer or as segments of propylene homopolymer. This absorption band is probably caused by an interaction of the vibrational modes of the methyl groups being on alternate carbon atoms of the polymer backbone. There are other examples of polymers with groups on alternate carbon atoms of the polymer backbone, such as polyisobutylene, which have absorption bands in this region of the spectrum.

As long as one is investigating block copolymers of ethylene and propylene, the use of the 1154 cm.$^{-1}$ band for the determination of propylene content is satisfactory. However, this is not the case for random copolymers.

Infrared spectra representative of the types of materials discussed are shown in the Figures 1-3.

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